KOKAI PATENT APPLICATION NO. SHO 54-52690

IMPROVED FLUORINE-CONTAINING CATION EXCHANGE FILM

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IMPROVED FLUORINE-CONTAINING CATION EXCHANGE FILM

[*Kairyohsareta ganfusso yoion kohkanmaku*]

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[*There are no amendments to this patent.*]

Specification

1. Title of the invention

Improved fluorine-containing cation exchange film

2. Claim of the invention

(1) A crosslinked fluorine-containing cation exchange film made of a copolymer comprising the iodide-containing vinyl ether (I) shown in general formula below

$$I(CF_2)_pO(CF_2CF_2O)_q(CF(CF_3)CF_2O)_rCF=CF_2$$

(Wherein, p is 2-9, q is 0-5, and r is 0-5), olefin fluoride (II), and a fluorine-containing monomer (III) having an ion exchange group or a functional group that can be converted to the aforementioned group.

(2) The film described in claim (1) in which the aforementioned olefin fluoride (II) is a

compound represented by the general formula $CF_2=CZZ^1$ (wherein, Z and Z^1 are fluorine, chlorine, hydrogen, or $-CF_3$).

(3) The film described in claim (1) in which the aforementioned fluorine-containing monomer containing an ion exchange group or a functional group that can be converted to the aforementioned group is a compound represented by the general formula

$$CF_2=CX(OCF_2CFY)_l(O)_m(CFY^1)_nA$$

(Wherein, X is either fluorine or $-CF_3$, Y and Y^1 are fluorine or perfluoroalkyl groups of 1-10 carbon atoms, and A is one of the ion exchange groups listed below $-SO_3H$, $-COOH$, $-PO_2H_2$, $-\phi OH$ (ϕ is an aryl group), $-C(CF_3)_2OH$ or a group that can be converted to the aforementioned ion exchange group. Furthermore, l is 0-3, m is either 0 or 1, and n is 0-12).

(4) The film described in claims (1), (2) or (3) in which the amount of iodide-containing vinyl ether in the aforementioned copolymer is in the range of 0.1-10 mol%.

(5) The film described in claims (1), (2), (3) or (4) in which the amount of iodide-containing vinyl ether in the aforementioned fluorine-containing monomer having an ion exchange group or a functional group that can be converted to the aforementioned group (III) is in the range of 1-50 mol%.

3. Detailed description of the invention

The present invention pertains to a fluorine-containing ion exchange film with improved electrochemical properties, in particular, mechanical properties. And the invention further pertains to a fluorine-containing ion exchange film characterized by the fact that the film is a copolymer comprising the iodide-containing vinyl ether (I) shown in general formula below

$$I(CF_2)_pO(CF_2CF_2O)_q(CF(CF_3)CF_2O)_rCF=CF_2$$

(Wherein, p is 2-9, q is 0-5, and r is 0-5), olefin fluoride (II) and fluorine-containing monomer (III) having an ion exchange group or a functional group that can be converted to the aforementioned group and having a crosslinked structure.

[p. 2]

In the past, a film comprising a copolymer of tetrafluoroethylene and perfluoro vinyl ether having a sulfonic acid group or carboxylic acid group and used as an ion exchange film has been proposed as described in publications such as Japanese Kokoku [Examined] Patent Application No. Sho 48-20788 and Japanese Kokoku [Examined] Patent Application No. Sho 48-41942. When a cation exchange film comprising the aforementioned copolymer of perfluoro vinyl ether and tetrafluoroethylene is used as a diaphragm of alkaline electrolysis, relatively good electrochemical properties can be achieved but significant changes in dimensions and formation of wrinkles takes place after extended operation, which cause a reduction in useful life of the aforementioned cation exchange film.

As a result of much research conducted by the present inventors in an effort to eliminate the above-mentioned change in dimensions and formation of wrinkles in the cation exchange film comprising the aforementioned copolymer of perfluoro vinyl ether and tetrafluoroethylene during the course of use without reducing the electrochemical properties, the inventors discovered that the aforementioned purpose could be achieved by a cation exchange film having a crosslinked structure made of a copolymer comprising the aforementioned specific monomer composition.

In the present invention, the aforementioned iodide-containing vinyl ether (I) shown in the general formula

$$I(CF_2)_pO(CF_2CF_2O)_q(CF(CF_3)CF_2O)_rCF=CF_2$$

(Wherein, p, q, and r are the same as above, and it is further desirable when p is 2-5, q is 0-3, and r is 0-3) is an essential component to achieve the aforementioned purpose, and when an iodide-containing compound without the aforementioned structure is used, an increase in the aforementioned mechanical properties is not possible and furthermore, it leads to deterioration in the electrochemical performance. The aforementioned iodide-containing vinyl ether (I) used in

the present invention can be produced by known methods, and for example, the described in Japanese Kokoku [Examined] Patent Application No. Sho 45-8205 can be used.

The aforementioned olefin fluoride (II) used in the present invention is represented by the general formula $CF_2=CZZ^1$ (wherein, Z and Z^1 are fluorine, chlorine, hydrogen, or $-CF_3$) and as typical examples, tetrafluoroethylene, trifluorochloroethylene, propylene hexafluoride, ethylene trifluoride, vinylidene fluoride, vinyl fluoride, etc. can be mentioned. In particular, a perfluoro compound is desirable and tetrafluoroethylene is especially desirable.

Furthermore, the aforementioned fluorine-containing monomer having an ion exchange group or a functional group that can be converted to the aforementioned group (III) used in the present invention is shown in the general formula below.

$$CF_2=CX(OCF_2CFY)_l(O)_m(CFY')_n-A$$

Wherein, l is 0-3, m is 0-1, n is 0-12, and X is either fluorine or CF_3, and Y and Y' are either fluorine or perfluoroalkyl groups of 1-10 carbon atoms. Furthermore, A is one of the ion exchange groups shown below, namely, $-SO_3H$, -COOH, $-PO_2H_2$, $-\phi OH$ (ϕ is aryl group), $C(CF_3)_2OH$ or a group that can be converted to one of the aforementioned ion exchange groups, for example, $-SO_2F$, $-SO_2Cl$, -CN, -COF, -COOR (R is an alkyl group of 1-10 carbon atoms), -COOM (M is an alkali metal or quaternary ammonium salt), etc. can be mentioned. The aforementioned fluorine-containing monomer (III) can be produced by known methods, for example, the method described in the specification of United States Patent 3282875, the method described in the specification of Japanese Kokoku [Examined] Patent Application No. Sho 45-22327, etc.

The aforementioned copolymer comprising iodide-containing vinyl ether (I), olefin fluoride (II), and fluorine-containing monomer having an ion exchange group (III) or a functional group that can be converted to the aforementioned group of the present invention can be produced as polymerization is conducted in the usual manner with or without an inert organic

solvent or an aqueous medium in the presence of a polymerization initiator such as a peroxy compound, azo compound, ultraviolet rays, or ionizing radiation.

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The amount of iodide-containing vinyl ether (I) included in the aforementioned copolymer is in the range of 0.1-10 mol%, preferably, 0.5-5 mol%. The amount of the fluorine-containing monomer having an ion exchange group (III) or a functional group that can be converted to the aforementioned group included in the aforementioned copolymer varies depending on the ion exchange capacity of the film, and is preferably in the range of 1-50 mol%, and especially, in the range of 5-25 mol%.

Crosslinking is provided for the aforementioned copolymer and it is desirable when film formation is provided prior to the crosslinking. The means used for film formation is not especially limited and for example, the press molding method, roll molding method, extrusion molding method, solution casting method, dispersion molding method, powder molding method, etc. may be used. The film produced as described above has a thickness in the range of 20-1,000 microns, preferably, in the range of 50-500 microns, and water permeation with a water column of 1 m (in 4N NaCl solution of pH 10 at 60°C) of 100 ml/hr/m^2 or below, preferably, 10 ml/hr/m^2 or below. The exchange capacity of the cation exchange film varies depending on the amount of the aforementioned fluorine-containing monomer (III) included, and when used as a diaphragm for alkaline electrolysis, 0.5-2.5 milliequivalents/gram dry resin, preferably, 0.7-2.0 milliequivalents/gram dry resin, is desirable.

The aforementioned copolymer is formed into a film right after the aforementioned film formation, and crosslinking of the copolymer of the present invention can be achieved by known means using common methods for crosslinking of standard linear polymers such as application of heat, ultraviolet rays, and radiation. For example, a method where heat is applied at approximately 250°C and crosslinking is done while removing the iodine generated under pressure.

When the aforementioned polymer does not include an ion exchange group but includes a functional group that can be converted into the aforementioned group, either a hydrolysis reaction or neutralization reaction is provided before or after the aforementioned film formation process or crosslinking process, preferably, after both processes, to convert the aforementioned functional group into an ion exchange group.

The cation exchange film comprising the aforementioned fluorine-containing copolymer having the aforementioned excellent electrical properties and mechanical properties can be used in a variety of fields.

For example, the aforementioned cation exchange film can be used effectively in fields where corrosion resistance is required such as electrolytic reduction, fuel cells, and diffusion dialysis. Especially when used as a diaphragm cell in an alkaline chloride, excellent performance can be expected.

Any known method can be used for production of the alkali hydroxide upon electrolysis of an alkali chloride using the aforementioned fluorine-containing cation exchange film. For example, for the electrolysis voltage and current density, preferably, 2.3-3.5 volts and 5-100 A/dm^2 can be used, respectively. For the anode used for electrolysis, a corrosion resistant electrode having high dimensional stability produced by coating an oxide of platinum metal onto a graphite base material or titanium base material can be used.

For example, when an anodic chamber and cathodic chamber are formed with the cation exchange film of the present invention and an alkali chloride solution is supplied to the anodic chamber and electrolysis is conducted so as to produce an alkali hydroxide in the cathodic chamber, production of a sodium hydroxide with a high concentration of at least 40% can be achieved at a low electrolysis voltage and high current efficiency without causing deterioration of the film when the electrolysis is performed at a temperature in the range of 40-100°C, preferably, 50-90°C under a current density in the range of 5-50 A/dm^2 using a sodium chloride solution with at least 2N concentration.

The present invention is explained further in specific terms with the working examples below, and needless to say, the present invention is not limited by these working examples.

It should be noted that exchange capacity of the fluorine-containing cation exchange film in working examples below was obtained as explained below. An H type cation exchange resin film is stored in 1N HCl for 5 hours at 60°C to completely convert it to H type and thorough washing was provided with water to eliminate the HCl completely. Furthermore, 0.5 g of the aforementioned H type film was dipped in a solution containing 25 ml of 0.1N NaOH and it was completely converted to Na+ type. Subsequently, the aforementioned film was removed and then, back titration was done for the amount of the NaOH included in the aforementioned solution using 0.1N hydrochloric acid.

[p. 4]

Working Example 1

37.5 g of $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, 6.3 g of $CF_2=CFO(CF_2)_4I$, 31.5 g of trichlorotrifluoroethane and 140 mg of azobisisobutylonitrile were charged to a 200 ml stainless steel reaction vessel. Subsequently, a thorough degassing was provided with liquid nitrogen [sic], after degassing the reactor temperature was increased to 70°C. Furthermore, 10.5 Kg/cm^2 of tetrafluoroethylene was charged and a reaction was conducted. As a result, 6.2 g of white copolymer was produced after 20 hours. The content of $CF_2=CFO(CF_2)_4I$ in the aforementioned copolymer was 2.6 mol% based on mass balance. Press molding was performed for the aforementioned copolymer at a temperature of 200°C to produce a film with a thickness of 200 μ, the film was then retained at 250°C for 6 hours under pressure as the iodine generated was removed and crosslinking was promoted. When a hydrolysis reaction was conducted for the aforementioned film, an ion exchange film with functional group content of 0.79 milliequivalents/g dry resin was produced.

Using the aforementioned ion exchange film, electrolysis was provided under the

conditions described below. Using Rh-Ti for the anode and stainless steel for the cathode, a two-chamber electrolysis tank (distance between electrodes 2.2 cm and film effective area 25 cm^2) was assembled. 4N NaCl solution was supplied to the anodic chamber at a rate of 150 cc/hr and a specific amount of water was supplied to the cathodic chamber in such a manner that an NaOH concentration of 8N could be achieved, and electrolysis was conducted at a current density of 20 A/cm^2 and liquid temperature of 85°C. As a result, 8N NaOH was achieved under a current efficiency of 70%. When the aforementioned electrolysis was continued for three months, the change in dimensions of the aforementioned ionic film was 0.7% and wrinkles formed were insignificant.

On the other hand, an ion exchange film having a functional group capacity of 0.78 milliequivalents/g produced by copolymerizing tetrafluoroethylene and

exhibited a change in dimensions of 4.5% after three months and formation of many wrinkles was observed.

Working Example 2

39.0 g of $CF_2=CFO(CF_2)_3COOCH_3$, 5.3 g of $CF_2=CFO(CF_2)_4I$ and 20 mg of azobisisobutylonitrile were charged to a 200 ml stainless steel reaction vessel. Subsequently, thorough degassing was provided with liquid nitrogen [sic], after degassing the reactor temperature was increased to 70°C. Furthermore, 19.5 Kg/cm^2 of tetrafluoroethylene was charged and a reaction was conducted. The pressure of the reaction system was maintained at 19.5 Kg/cm^2 during the course of the reaction as tetrafluoroethylene was introduced. As a result, 6.9 g of copolymer was produced after 5 hours. The content of $CF_2=CFO(CF_2)_4I$ in the aforementioned copolymer was 2.2 mol% based on mass balance.

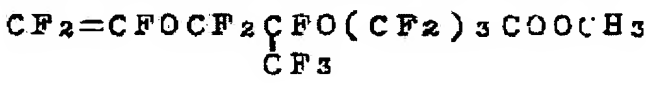
Furthermore, press molding was conducted for the aforementioned copolymer at a temperature of 200°C to produce a film with a thickness of 200 μ, the film was then retained at 250°C for 6 hours under pressure as the iodine generated was removed and crosslinking was

promoted. When a hydrolysis reaction was conducted for the aforementioned film, an ion exchange film with functional group content of 1.45 milliequivalents/g was produced. The aforementioned electrolysis described in Working Example 1 was done using the aforementioned ionic film. As a result, 14N NaOH was achieved under a current efficiency of 93%. When the aforementioned electrolysis was continued for three months, the change in dimensions of the aforementioned ionic film was 0.8% and the wrinkles formed were insignificant.

On the other hand, an ion exchange film having a functional group capacity of 1.45 milliequivalents/g produced by copolymerizing tetrafluoroethylene and $CF_2=CFO(CF_2)_3COOCH_3$ exhibited a change in dimensions of 4.0% after three months and formation of many wrinkles was observed.

Working Example 3

Under the conditions described in the Working Example 2 above, copolymerization was conducted for tetrafluoroethylene and



and $CF_2=CFO(CF_2)_4I$ and crosslinking was further performed to produce an ion exchange film with a $CF_2=CFO(CF_2)_4I$ content of 2.9 mol% and a functional group capacity of 1.29 milliequivalents/g dry resin. When electrolysis was conducted with the amount ionic film according to the conditions described in Working Example 1 above, 14N NaOH was achieved under current efficiency of 92%. When the aforementioned electrolysis was continued for three months, the change in dimensions of the aforementioned ionic film was 0.7% and wrinkles formed were insignificant.

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